Structural and Electrical Studies of Electrohydrodynamic Atomized ITO Thin Films

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Abstract. Indium Tin Oxide thin films have been fabricated through electrohydrodynamic atomization, an advanced direct printing technique. Optimization of the process parameters such as flow rate, applied voltage, nozzle to substrate distance and substrate speed which play crucial roles in determining the thickness and morphology of the thin films are detailed. XRD results ensured the purity of ITO thin films thus deposited. FE-SEM analysis was employed to study the surface morphology. UV-vis spectrum of ITO thin film showed transmittance of above 95%. Electrical study revealed Ohmic behavior of ITO thin films.

Introduction

Indium tin oxide (ITO) is a highly transparent, wide band gap semiconducting material with a good conductivity. Owing to its optical band gap of 3.6 eV, ITO has found its application as an advanced transparent semiconducting material in the opto-electronics industry [1-4]. The high conductivity is observed only in non-stoichiometric form of ITO resulting from the oxygen deficiency and dopant tin(Sn), whereas the stoichiometric form acts as an insulator [5]. Further, the structural, optical and electrical properties also depend on the fabrication techniques adopted and the growth conditions which could be maneuvered [6]. Thus far, ITO thin films have been prepared by a wide range of deposition techniques which include sputtering[7], reactive thermal evaporation[8], electron beam evaporation[4], plasma enhanced metallorganic chemical vapor deposition (PEMOCVD) [9], laser ablation [10], ion assisted deposition [11] and pulsed laser deposition [12]. Physical vapour deposition techniques have been reported to yield good quality ITO thin films and offer controllability over the thin films produced.

In this present study, we have fabricated ITO thin films through electrohydrodynamic atomization (EHDA) which is a cost-effective, room temperature, direct printing process and one of the developing fabrication techniques in the field of printed electronics [13]. The structural, optical and electrical properties of the deposited ITO thin films are discussed here.

Experimental

ITO thin films have been produced through electrohydrodynamic atomization at room temperature and atmospheric pressure. The basic principle of EHDA depends on the disruption of liquid into an atomized spray due to the applied electric field. A liquid precursor is fed to a nozzle and on the application of electric field droplets at the nozzle tip form a stable cone-jet also known as Taylor cone. The charged, stable cone-jet of liquid precursor reaches the substrate as spray containing fine, charged liquid droplets. The substrate either carries a charge opposite to the droplet or grounded [13]. EHDA technique can deposit thin films of a wide range of organic, inorganic compounds and synthetic polymers. The process can retain the samples relatively free from damage, as the process is carried out under room temperature and atmospheric pressure. This technique is capable of processing nano particles and fibers to deposit thin films over a large area.
and can be incorporated with roll-to-roll systems for mass production. Furthermore, depositions and patterns of the particle can be controlled by tuning the process parameters. ITO ink of 5wt% was prepared by dispersing ITO nanoparticles in a combination of ethanol and deionized water upon stirring with Triton-100x as the surfactant. The solution was stirred for 5 hours to achieve a stable, homogeneous dispersion. PES substrates have been cleaned using de-ionized water and isopropanol in ultrasonic agitator and plasma treated for enhanced adhesion prior to the deposition.

A constant flow rate (100 μl/hr) of the ITO ink was maintained throughout the deposition by a syringe pump (Harvard Apparatus, PHD 2000 Infusion) which held a syringe (Hamilton, Model 1001GASTIGHT syringe) containing the ink. The ITO (5 wt%) ink was sprayed through 150μm stainless steel nozzle (NanoNC, NNC-DN-2230). A high-voltage regulated DC power supply (NanoNC) connected between the nozzle and the copper plate ground electrode was used to supply 5.0kV voltage throughout the deposition. Distance between the substrate and nozzle was maintained at 7mm. A high resolution CCD camera (MotionPro N3) capable of operating at high speeds was employed to observe the tip of the nozzle in order to capture various modes of the liquid flow. The deposited ITO thin films were then annealed at 120 ºC.

Figure 1 shows the X-ray diffraction pattern of ITO thin films fabricated through EHDA. The predominant plane was (222) in addition to the peaks of (211), (400) and (440) which verify the cubic structure of In2O3. The peak (123) corresponding to the cassiterite phase of SnO2 could also be seen in the diffractogram with low intensity peaks of ITO phase namely (411), (431) and (611) [14]. The XRD spectrum validates the purity and crystallinity of ITO thin films fabricated through EHDA despite the process being carried out at room temperature.

The crystallinity and purity of ITO thin films were analyzed using an X-ray diffractometer (Rikagu D/MAX 2200H, Bede model 200). The XRD measurement was performed using a Cu Kα radiation source of wavelength λ = 1.5406 Å. Transmittance of the ITO thin films was recorded by a UV-vis spectrometer (Shimadzu UV-3150) with a wavelength range of 200–800 nm. The surface morphology was examined by a field emission scanning electron microscope (FE-SEM, JSM-6700F, JEOL Ltd). The current-voltage (I-V) characteristics were measured by a semiconductor device (B1500A, Agilent, USA) parameter analyzer.

Results and discussion

Figure 1 shows the X-ray diffraction pattern of ITO thin films fabricated through EHDA. The predominant plane was (222) in addition to the peaks of (211), (400) and (440) which verify the cubic structure of In₂O₃. The peak (123) corresponding to the cassiterite phase of SnO₂ could also be seen in the diffractogram with low intensity peaks of ITO phase namely (411), (431) and (611) [14]. The XRD spectrum validates the purity and crystallinity of ITO thin films fabricated through EHDA despite the process being carried out at room temperature.
Figure 2 shows the FE-SEM micrographs of ITO thin films at different magnifications. The micrographs reveal the surface morphological features of ITO thin films. The thin films found to have well connected nanocrystallites of uniform size. The surface of ITO thin films was densely packed and smooth which meet the requirements of electrode applications.

Figure 3 shows the transmittance UV-vis spectrum of ITO thin films. The wavelength range was set between 200nm to 800nm to record the transmittance spectrum. The transmittance value of ITO thin films at Fraunhofer sodium D-line (589.59 nm) was found to be 96% which qualifies the deposited ITO thin films as highly transparent. The cut-off wavelength found in the UV-vis spectrum at 50% transmittance was well below 350 nm which substantiates that ITO is completely colourless.

Figure 4 shows the I-V characteristics of the ITO thin films. The current-voltage characteristics was studied from -5V to 5V applied voltages. The I-V curves showed perfectly linear behaviour through the origin. This Ohmic behaviour exhibited by the ITO thin films demonstrates the conducting nature and potential application as electrodes in a wide range of electronic devices.

Conclusion

ITO thin films have been fabricated by a cost-effective, room temperature, advanced direct printing technique of EHDA. The XRD analysis confirmed the purity and crystalline nature of ITO thin films implying the process introduced no impurities. Surface morphology of the thin films revealed smooth surface with densely packed nanocrystallites of uniform size. The optical studies showed that ITO is colourless and highly transparent with a transparency of 96%. Perfectly Ohmic behaviour of current-voltage curve validated the conducting nature of ITO thin films. The electrohydrodynamic atomization technique with its flexibility to incorporate with roll to roll systems has the potential to mass produce feasible, high purity thin films at higher production rates without any need for isolated ambience. The ITO thin film thus produced through this technique is a promising candidate to be used as highly transparent electrodes in energy storage applications, organic photovoltaics, organic light emitting diodes and in sensor modules.

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References


